



SEPA

Project Summary

EPA Method Study 30, Method 625 — Base/Neutrals, Acids and Pesticides

The work described in the report was performed to validate, proposed Method 625 for the analysis of the base/neutral (B/N), acid, and pesticide priority pollutants, through an interlaboratory study. This method is based on the extraction and concentration of the various analytes followed by their determination through gas chromatography (GC) using a low resolution mass spectrometer (MS) as the measuring device.

Participating laboratories were selected based upon technical evaluation of proposals and upon the analytical results of prestudy samples. The laboratories were supplied ampules containing various concentrations of the pollutant compounds. These solutions were aliquoted into four different water types and analyzed according to the method. In addition to the sample concentrates, each laboratory was supplied with an industrial effluent containing various organic pollutants to determine the method's propensity to produce false positive and false negative results.

The data obtained from the interlaboratory study were analyzed employing a series of EPA computer programs known as the Interlaboratory Method Validation Study (IMVS) system which was designed to implement ASTM procedure D2777. The IMVS system includes tests for the rejection of outliers (both laboratory and individual), estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and precision.

This Project Summary was developed by EPA's Environmental Monitoring

and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The analytical laboratories of the U.S. Environmental Protection Agency (EPA) gather water quality data to provide information on water resources, to assist research activities, and to evaluate pollution abatement activities. The success of these pollution control activities depends upon the reliability of the data provided by the laboratories, particularly when legal action is involved.

The Environmental Monitoring and Support Laboratory-Cincinnati (EMSL-Cincinnati), of the EPA develops analytical methods and conducts a quality assurance program for water and waste laboratories. The EMSL quality assurance program is designed to maximize the reliability and legal defensibility of water quality information collected for and by EPA laboratories. The responsibility for EMSL's quality assurance activities is assigned to the Quality Assurance Branch (QAB), which conducts interlaboratory tests of the methods. This study reports the results of the validation effort on Method 625 for the base/neutral, pesticide, and acid compounds.

The interlaboratory study of method 625 consisted of three distinct phases. Phase I involved the preparation of concentrates, ampuling of the concentrates, and analytical verification of the true values for analytes in the concentrates, using GC methods.

Phase II involved the selection of participating laboratories. Solicitations were made for paid participants and volunteer participants. Selection of laboratories was based on experience, facilities, quality control procedures, and cost estimates received from laboratories. Final selection of 15 laboratories was made after their successful analysis of a performance sample. No laboratories chose to participate in the study as volunteers.

Phase III involved conducting the formal method validation study. The prepared ampules were distributed to each laboratory. Individual laboratories supplied the required four water types (distilled water, tap water, surface water and industrial effluent) into which the ampules were to be spiked. As a separate study, a single industrial wastewater was supplied by Radian to evaluate the analysis of a very diffucult sample (including tendencies for false-positives and false-negatives). After analyses, results were reported on standard data sheets. Data were keypunched and validated by Radian. The final step in the study was to conduct an analysis of all data obtained using the IMVS computer program.

Procedure

The design of the interlaboratory study of Method 625 was based on the nonreplicate technique by W.J. Youden. According to this technique, samples are prepared in pairs at several levels of concentration where the concentration of each analyte in a sample pair is slightly different. The analyst is directed to perform a single analysis and report one value for each analyte in the sample.

Sample pairs for each method were prepared at low, medium and high levels within the linear range of the MS and constituted three Youden pairs. However, because of the number of analytes present, the base/neutral-containing ampules were divided into two groups of three paris for a total of 12 separate base/neutral ampules.

The samples were prepared as concentrates in sealed ampules and shipped to the participating laboratories. Each laboratory was responsible for supplying laboratory pure water, finished drinking water, a surface water, and an industrial or municipal effluent water for each concentrate to a volume of water from each of the four water types and subsequently to analyze the spiked water samples.

In addition to the sample ampules, an industrial effluent water selected by

Radian was furnished to each participating laboratory for analysis. This sample was known to contain a number of the priority pollutants and was judged to be difficult to analyze. The purpose of the industrial effluent sample was to evaluate Method 625 on false positive and false negative results.

After analyses were completed, the results were subjected to statistical analyses using EPA's IMVS computer programs to determine the precision and accuracy of Method 625.

Results and Discussion

The objective of this interlaboratory study was to characterize the performance of Method 625 in terms of accuracy, overall precision, single-analyst precision, and the effect of water type on accuracy and precision. Through statistical analyses of 22,555 reported values, estimates of accuracy and precision were made and expressed in regression equations for each compound. The equations shown in Table 1-1 through 1-17 were based on the 17,998 data values remaining after eliminating outliers in the IMVS program. Table 2 represents revised equations for two compounds. The development and interpretation of these regression equations are discussed in Section 5 of the main report.

The accuracy is obtained by comparing the mean recovery to the prepared values of the concentrations and computing the percent recovery. The mean recovery statistics (at 100 µg/L) for the base/neutral compounds range from 21% for dimethyl phthalate to 113% for isophorone. The average recovery is 74%. Both of these extremes are for the distilled water matrix. The mean recovery for 3,3'dichlorobenzidine in the industrial effluent matrix is also 113%. One-half of the mean recoveries for the base/neutral compounds are between 61% and 87%. with one-fourth of the mean recoveries above and below these values. Recoveries for dimethyl phthalate are consistently low, ranging from 21% to 34%, for all water matrices.

The mean recovery statistics (at 100 µg/L) for the acid compounds range from 44% for phenol to 106% for 2-nitrophenol with an average value of 74%. These extremes are for the distilled water and are between 59% and 87%, with one-fourth of the mean recoveries above and below these values. Recoveries for 2-nitrophenol are very good for all water matrices with mean recoveries, ranging from 91% to 106%. Mean recoveries for phenol and 4-nitrophenol are consistently low (probably due to loss of these

compounds into the base/neutral fraction) with recoveries ranging from 44% to 48% and 54% to 60%, respectively. The phthalates, particularly dimethyl and diethyl phthalate, may have hydrolyzed when the water samples were made basic for the base/neutral extraction. thus contributing to low recovery. In general, one would expect the lower molecular weight phthalate esters to hydrolyze more rapidly than the higher molecular weight esters. The high overall recoveries for isophorone could be partially due to the poor chromatography of this compound on the packed GC column, contributing to nonlinear response in the mass spectrometer.

The overall standard deviation of the analytical results is an indication of the precision associated with the measurement generated by a group of laboratories. The percent relative standard deviation (RSD) at 100 μ g/L for the base/neutral compounds range from 10% for phenanthrene in the tap water matrix to 104% for dimethyl phthalate in the surface water matrix with a median value of 35%. Precision for dimethyl phthalate is poor for all water matrices with RSDs ranging from 88% to 104%. One-half of the RSDs for the base/neutral compounds are between 26% and 52%. In 95% of the cases, the RSDs are less than 76%. The RSDs (at $100 \mu g/L$) for the acid compounds range form 21% for 2,4,6-trichlorophenol in the tap water matrix to 91% for 2.4dinitrophenol in the distilled water matrix with a median RSD of 32%. Precision for 2,4-dinitrophenol is poor for all water matrices with RSDs ranging from 68% to 91%. One-half of the RSDs for the acid compounds are between 27% and 47%. In 95% of the cases the RSDs are less

The percent relative standard deviation for a single analyst (RSD-SA) indicates the precision associated with a single laboratory. The RSD-SA for base/neutral samples at 100 µg/L ranges from 8% for 2-chloronaphthalene in the distilled water matix to 72% for dimethyl phthalate in the surface water matrix, with a median RSD-SA of 24%. With the exception of the tap water matrix, singleanalyst precision for dimethyl phthalate is poor with RSD-SAs ranging from 55% to 72%. One-half of the RSD-SAs for the base/neutral compounds at 100 µg/L are between 18% and 34%. In 95% of the cases, the RSD-SAs are less than 51%.

The RSD-SAs (at $100 \,\mu\text{g/L}$) for the acid compounds range from 12% for 2,4,6-trichlorophenol in the industrial effluent matrix to 45% for 2,4-dinitrophenol in the tap water matrix with a median RSD-SA

Water Type	Acenaphthene	Acenaphthylene	Aldrin	Anthracene
Applicable Conc. Range -μg/L	(7.0 - 400.0)	(8.0 - 450.0)	(11.0 - 600.0)	(5.0 - 600.0)
Distilled Water				
Single-Analyst Precision	SR = 0.15X - 0.12	SR = 0.24X - 1.06	SR = 0.27X - 1.28	SR = 0.21X - 0.32
Overall Precision	S = 0.21X - 0.67	S = 0.26X - 0.54	S = 0.43X + 1.13	$S = 0.27X \cdot 0.64$
Accuracy	X = 0.96C + 0.19	X = 0.89C + 0.74	X = 0.78C + 1.66	X = 0.80.C + 0.68
Tap Water				
Single-Analyst Precision	SR = 0.09X + 0.56	SR = 0.16X + 0.37	SR = 0.28X - 0.48	SR = 0.15X - 0.17
Overall Precision	S = 0.17X + 0.10	S = 0.23X - 0.25	S = 0.47X - 0.92	S = 0.19X - 0.07
Accuracy	X = 0.95C + 0.08	X = 0.87C + 0.48	X = 0.66C + 0.88	X = 0.82C + 0.42
Surface Water				
Single-Analyst Precision	SR = 0.21X - 0.60	SR = 0.14X - 0.01	SR = 0.36X - 1.64	SR = 0.18X + 0.02
Overall Precision	S = 0.27X - 0.02	S = 0.21X + 0.67	S = 0.52X - 1.01	S = 0.24X - 0.11
Accuracy	X = 0.91C - 0.02	X = 0.97C + 0.24	X = 0.55C + 1.00	X = 0.81C + 0.55
Industrial Effluent				
Single-Analyst Precision	SR = 0.15X - 0.07	SR = 0.13X - 0.35	SR = 0.38X + 0.17	SR = 0.17X - 0.03
Overall Precision	S = 0.18X + 0.38	S = 0.25X - 0.44	S = 0.59X + 0.08	S = 0.29X + 0.13
Accuracy	X = 0.85C + 0.46	X = 0.88C - 0.03	X = 0.52C + 0.80	X = 0.74C + 0.88

Table 1-2. Regression Equations for Accuracy and Precision for Compounds 5

Water Type	B-8HC	Benzo(A)Anthracene	Benzo(A)Pyrene	Benzo(B)Fluoranthene
Applicable Conc. Range -µg/L	(14.0 - 750.0)	(18.0 - 400.0)	(5.0 - 600.0)	(11.0 - 600.0)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.20X - 0.58 S = 0.30X - 1.94 X = 0.87C - 0.94	SR = 0.15X + 0.93 S = 0.26X - 0.28 X = 0.88C - 0.60	SR = 0.22X + 0.48 S = 0.32X + 1.35 X = 0.90C - 0.13	SR = 0.22X + 0.43 S = 0.29X + 0.96 X = 0.93C - 1.80
Tap Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.16X - 0.14 S = 0.22X - 0.77 X = 0.81C - 0.43	SR = 0.19X + 4.78 S = 0.26X + 2.49 X = 0.80C + 1.14	SR = 0.33X + 0.38 S = 0.40X + 0.35 X = 0.79C - 0.95	SR = 0.32X + 1.01 S = 0.45X + 1.04 X = 0.70C - 1.73
Surface Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.15X - 0.72 S = 0.23X - 0.39 X = 0.80C - 0.44	SR = 0.32X - 1.44 S = 0.36X - 0.63 X = 0.71C - 0.22	SR = 0.39X + 0.75 S = 0.45X + 0.71 X = 0.68C - 0.04	SR = 0.35X - 0.42 S = 0.42X + 0.82 X = 0.66C - 1.40
Industrial Effluent Single-Analyst Precision Overall Precision Accuracy	SR = 0.17X - 0.16 S = 0.25X - 0.23 X = 0.84C - 0.89	SR = 0.43X - 1.81 S = 0.53X - 0.46 X = 0.63C - 0.79	SR = 0.41X - 0.12 S = 0.65X + 0.09 X = 0.56C - 0.26	SR = 0.41X - 0.40 S = 0.62X - 0.08 X = 0.56C - 0.48

Table 1-3. Regression Equations for Accuracy and Precision for Compounds 9

Water Type	Bis(2-Chloroethyl)Ether	Di-N-Butylphthalate	Dibenzo(A,H)Anthracene	Diethyl Phthalate
Applicable Conc. Range -μg/L	(14.0 - 750.0)	(6.0 - 700.0)	(9.0 - 400.0)	(6.0 - 700.0)
Distilled Water				
Single-Analyst Precision	SR = 0.35X - 0.99	SR = 0.13X + 0.16	SR = 0.30X + 8.51	SR = 0.28X + 1.44
Overall Precision	S = 0.35X + 0.10	S = 0.39X + 0.60	S = 0.59X + 0.25	S = 0.52X + 0.22
Accuracy	X = 0.86C - 1.54	X = 0.59C + 0.71	X = 0.88C + 4.72	X = 0.43C + 1.00
Tap Water				
Single-Analyst Precision	SR = 0,25X + 1.49	SR = 0.24X + 0.19	SR = 0.38X + 0.17	SR = 0.34X + 0.11
Overall Precision	S = 0.27X + 1.79	S = 0.34X - 0.12	S = 0.55X - 0.26	S = 0.65X - 0.20
Accuracy	X = 0.87C - 2.52	X = 0.59C + 0.40	X = 0.85C - 4.72	X = 0.43C + 0.37
Surface Water				
Single-Analyst Precision	SR = 0.26X - 1.07	SR = 0.27X - 0.69	SR = 0.37X - 0.02	SR = 0.40X + 0.77
Overall Precision	S = 0.32X + 0.58	S = 0.34X + 0.84	S = 0.50X + 0.13	S = 0.50X + 0.44
Accuracy	X = 0.89C - 1.02	X = 0.60C + 1.83	X = 0.64C - 1.44	X = 0.51C + 1.29
Industrial Effluent				
Single-Analyst Precision	SR = 0.21X + 3.15	SR = 0.23X + 0.32	SR = 0.45X - 0.76	SR = 0.33X - 0.05
Overall Precision	S = 0.34X + 0.69	S = 0.47X - 0.18	S = 0.86X - 0.49	S = 0.45X + 0.20
Accuracy	X = 0.91C - 0.72	X = 0.58C + 0.42	X = 0.63C - 2.51	X = 0.57C - 0.19

X = Mean Recovery C = True Value for the Concentration

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Water Type	Endosulfan Sulfate	Fluoranthene	Heptachlor	Hexachlorobenzena
Applicable Conc. Range -μg/L	(14 0 - 750.0)	(6.0 - 700.0)	(11.0 - 600.0)	(6.0 - 535.0)
Distilled Water				
Single-Analyst Precision	SR = 0.12X + 2.47	SR = 0.22X - 0.73	SR = 0.24X - 0.56	SR = 0.18X - 0.10
Overall Precision	S = 0.63X - 1.03	S = 0.28X - 0.60	S = 0.50X - 0.23	S = 0.43X - 0.52
Accuracy	X = 0.39C + 0.41	X = 0.81C + 1.10	X = 0.87C - 2.97	X = 0.74C + 0.66
Tap Water				
Single-Analyst Precision	SR = 0.20X + 1.28	SR = 0.12X + 0.93	SR = 0.37X - 0.68	SR = 0.25X + 0.15
Overall Precision	S = 0.66X - 0.60	S = 0.22X + 0.12	S = 0.44X - 0.17	S = 0.30X + 0.19
Accuracy	X = 0.68C - 4.82	X = 0.76C + 0.84	X = 0.73C - 2.31	X = 0.72C + 0.20
Surface Water				
Single-Analyst Precision	SR = 0.22X - 0.86	SR = 0.23X - 0.70	SR = 0.38X - 1.70	SR = 0.23X - 0.52
Overall Precision	S = 0.67X - 2.55	S = 0.29X - 0.64	S = 0.50X - 1.20	S = 0.32X - 0.22
Accuracy	X = 0.63C - 1.95	X = 0.71C + 1.15	X = 0.73C - 2.07	X = 0.69C + 0.65

SR = 0.19X + 0.73 S = 0.36X + 0.17 X = 0.68C + 1.53

SR = 0.39X - 0.95S = 0.49X + 0.09X = 0.68C - 1.44 SR = 0.17X + 0.14 S = 0.38X - 0.52 X = 0.58C + 0.22

Accuracy

Industrial Effluent

Single-Analyst Precision Overall Precision

 Table 1-5.
 Regression Equations for Accuracy and Precision for Compounds 17

SR = 0.40X - 0.24 S = 0.70X - 0.34 X = 0.65C - 4.67

Water Type	Isophorone	Naphthalene	PCB-1260	1,3-Dichlorobenzene
Applicable Conc. Range -µg/L	(5.0 - 600.0)	(6.0 - 700.0)	(36.0 - 667.0)	(5.0 - 600.0)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.27X + 0.77 S = 0.33X + 0.26 X = 1.12C + 1.41	SR = 0.21X - 0.41 S = 0.30X - 0.68 X = 0.76C + 1.58	SR = 0.35X + 3.61 S = 0.43X + 1.82 X = 0.81C - 10.86	SR = 0.25X + 0.68 S = 0.41X + 0.11 X = 0.86C - 0.70
Tap Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.30X - 0.22 S = 0.52X - 0.34 X = 1.10C + 2.07	SR = 0.18X - 0.36 S = 0.24X - 0.34 X = 0.77C + 1.28	SR = 0.50X - 2.60 S = 0.51X + 4.39 X = 0.68C - 17.11	SR = 0.24X + 0.90 S = 0.42X - 0.03 X = 0.89C - 1.10
Surface Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.20X + 1.36 S = 0.35X + 0.94 X = 1.05C + 0.65	SR = 0.24X - 0.84 S = 0.27X - 0.09 X = 0.78C + 1.39	SR = 0.72X - 4.51 S = 0.65X - 1.11 X = 0.51C - 11.95	SR = 0.32X + 0.14 S = 0.34X - 0.15 X = 0.92C - 0.86
Industrial Effluent Single-Analyst Precision Overall Precision Accuracy	SR = 0.42X - 3.27 S = 0.57X + 0.64 X = 1.00C + 9.41	SR = 0.20X - 0.18 S = 0.33X - 0.51 X = 0.70C + 1.82	SR = 0.43X + 2.02 S = 0.57X - 0.49 X = 0.46C - 12.56	SR = 0.33X + 0.49 S = 0.41X + 0.73 X = 0.79C - 0.27

Table 1 - 6. Regression Equations for Accuracy and Precision for Compounds 21

Water Type	2,6-Dinitrotoluene	3,3-Dichlorobenzidine	4-Chiorophenyi Phenyi Ether	4,4 -DDD
Applicable Conc. Range -μg/L	(11.0 - 600.0)	(36.0 - 667.0)	(9.0 - 500.0)	(7.0 - 400.0)
Distilled Water				
Single-Analyst Precision	SR = 0.14X + 1.26	SR = 0.28X + 7.33	SR = 0.20X - 0.94	SR = 0.29X - 0.32
Overall Precision	S = 0.19X + 0.35	S = 0.47X + 3.45	S = 0.30X - 0.46	S = 0.66X - 0.96
Accuracy	X = 1.06C - 3.60	X = 1.23C - 12.65	X = 0.91C + 0.53	X = 0.56C - 0.40
Tap Water				
Single-Analyst Precision	SR = 0.18X + 0.20	SR = 0.23X + 4.38	SR = 0.15X - 0.28	SR = 0.31X + 0.64
Overall Precision	S = 0.21X - 0.01	S = 0.44X + 5.46	S = 0.25X - 0.26	S = 0.55X - 0.33
A <i>ccuracy</i>	X = 1.02C - 2.81	X = 1.11C - 12.56	X = 0.95C + 0.04	X = 0.54C - 0.16
Surface Water				
Single-Analyst Precision	SR = 0.20X + 0.75	SR = 0.65X - 11.31	SR = 0.15X - 0.43	SR = 0.45X - 1.47
Overall Precision	S = 0.26X + 2.25	S = 0.70X - 9.34	S = 0.25X - 0.68	S = 0.68X - 1.33
Accuracy	X = 1.06C - 3.52	X = 1.22C - 20.68	X = 0.97C + 0.65	X = 0.49C + 0.31
Industrial Effluent				
Single-Analyst Precision	SR = 0.27X - 1.66	SR = 0.23X + 7.55	SR = 0.19X - 0.20	SR = 0.45X - 0.55
Overall Precision	S = 0.31X + 0.53	S = 0.42X + 0.78	S = 0.35X - 1.34	S = 0.58X - 0.79
Accuracy	X = 1.05C - 1.78	X = 1.33C - 20.41	X = 0.81C + 0.42	X = 0.46C - 0.38

X = Mean Recovery C = True Value for the Concentration

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Table 1-7. Reg	ression Equations for Accuracy and I	Precision for Compounds 25
Water Type		4,4 -DDE
Applicable Conc. R	ange -µg/L	(14.0 - 750.0)
Distilled Water Single-Analyst Pre Overall Precision Accuracy	cision	SR = 0.26X - 1.17 S = 0.39X - 1.04 X = 0.70C - 0.54
Tap Water Single-Analyst Pre Overall Precision Accuracy	cision	SR = 0.35X+0.38 S = 0.38X-0.14 X = 0.57C-0.28
Surface Water Single-Analyst Pre Overall Precision Accuracy	cision	SR = 0.21 X - 0.44 S = 0.39 X - 1.06 X = 0.47 C - 0.30
Industrial Effluent Single-Analyst Pre Overall Precision Accuracy	cision	SR = 0.39X+0.37 S = 0.49X-0.47 X = 0.47C+0.03

Table 1-8. Regression Equations for Accuracy and Precision for Compounds 1

Water Type	Benzo(G,H,I)Perylene	Benzo(K)Fluoranthene	Benzyl Butyl Phthalate	Bis(2-Chloroethoxy)Methane
Applicable Conc. Range -µg/L	(7.4 - 292.0)	(7.2 - 548.0)	(7.2 - 548.0)	(11.0 - 646.0)
Distilled Water				
Single-Analyst Precision	SR = 0.29X + 2.40	SR = 0.19X + 1.03	SR = 0.18X + 0.94	SR = 0.16X + 1.34
Overall Precision	S = 0.51X - 0.44	S = 0.35X + 0.40	S = 0.53X + 0.92	S = 0.26X + 2.01
Accuracy	X = 0.98C - 0.86	X = 0.87C - 1.56	X = 0.66C - 1.68	X = 1.12C - 5.04
Tap Water				
Single-Analyst Precision	SR = 0.43X - 1.02	SR = 0.20X - 0.17	SR = 0.17X + 2.17	SR = 0.15X + 2.85
Overall Precision	S = 0.54X - 0.85	S = 0.36X + 0.39	S = 0.52X + 1.34	S = 0.26X + 2.75
Accuracy	X = 0.70C - 1.79	X = 0.65C - 0.64	X = 0.61C - 0.26	X = 1.05C - 4.58
Surface Water				
Single-Analyst Precision	SR = 0.47X + 0.39	SR = 0.39X + 0.69	SR = 0.51X - 0.33	SR = 0.32X - 0.34
Overall Precision	S = 0.64X - 0.53	S = 0.55X + 0.48	S = 0.61X + 0.29	S = 0.33X + 1.28
Accuracy	X = 0.65C - 2.98	X = 0.63C - 0.44	X = 0.52C - 0.65	X = 0.95C - 2.98
Industrial Effluent				
Single-Analyst Precision	SR = 0.35X - 0.02	SR = 0.27X + 0.89	SR = 0.51X - 0.39	SR = 0.23X + 2.70
Overall Precision	S = 0.68X - 0.12	S = 0.64X + 0.22	S = 0.57X + 0.75	S = 0.30X + 1.76
Accuracy	X = 0.60C - 1.71	X = 0.54C + 0.56	X = 0.62C + 0.21	X = 1.01C + 0.12

Table 1-9. Regression Equations for Accuracy and Precision for Compounds 5

Water Type	Bis(2-Chloroisopropyl)Ether	Bis(2-Ethylhexyl)Phthalate	Chrysene	D-BHC
Applicable Conc. Range -µg/L	(14.0 - 508.0)	(7.2 - 548 0)	(5.4 - 411.0)	(7.2 - 547.0)
Distilled Water				
Single-Analyst Precision	SR = 0.24X + 0.28	SR = 0.26X + 0.73	SR = 0.28X + 0.13	SR = 0.34X + 0.86
Overall Precision	S = 0.25X + 1.04	S = 0.36X + 0.67	S = 0.33X - 0.09	S = 0.93X - 0.17
Accuracy	X = 1.03C - 2.31	X = 0.84C - 1.18	X = 0.93C - 1.00	X = 0.29C - 1.09
Tap Water				
Single-Analyst Precision	SR = 0.15X + 1.23	SR = 0.27X + 0.50	SR = 0.17X + 0.80	SR = 0.20X + 0.75
Overall Precision	S = 0.28X + 0.70	S = 0.48X + 0.44	S = 0.25X + 0.62	S = 0.91X - 0.14
Accuracy	X = 0.93C - 1.95	X = 0.63C - 2.33	X = 0.80C - 0.55	X = 0.35C - 0.75
Surface Water				
Single-Analyst Precision	SR = 0.33X - 1.59	SR = 0.39X - 0.45	SR = 0.35X - 0.14	SR = 0.62X - 2.52
Overall Precision	S = 0.30X + 1.21	S = 0.49X - 0.17	S = 0.44X - 0.21	S = 0.90X - 0.67
Accuracy	X = 0.85C + 0.87	X = 0.51C - 1.81	X = 0.62C + 0.16	X = 0.33C - 0.91
Industrial Effluent				
Single-Analyst Precision	SR = 0.12X + 0.88	SR = 0.32X + 0.69	SR = 0.33X + 0.28	SR = 0.32X + 0.95
Overall Precision	S = 0.21X + 0.09	S = 0.64X + 0.13	S = 0.52X + 0.14	S = 0.78X - 0.35
Accuracy	X = 0.95C + 0.13	X = 0.52C - 0.94	X = 0.66C + 0.27	X = 0.42C + 0.23

X = Mean Recovery C = True Value for the Concentration

X = Mean Recovery C = True Value for the Concentration

X = Mean Recovery C = True Value for the Concentration

Water Type	Di-N-Octylphthalate	Dieldrin	Dimethyl Phthalate	Endrin Aldehyde
Applicable Conc. Range -μg/L	(7.2 - 548.0)	(7.2 - 548.0)	(4.5 - 343.0)	(22.0 - 658.0)
Distilled Water				
Single-Analyst Precision	SR = 0.21X + 1.19	SR = 0.20X - 0.16	SR = 0.54X + 0.19	SR = 0.18X + 3.91
Overall Precision	S = 0.37X + 1.19	S = 0.26X - 0.07	S = 1.05X - 0.92	S = 0.73X - 0.62
Accuracy	X = 0.76C - 0.79	X = 0.82C - 0.16	X = 0.20C + 1.03	X = 0.76C - 3.86
Tap Water				
Single-Analyst Precision	SR = 0.26X + 0.52	SR = 0.20X - 0.46	SR = 0.27X + 0.08	SR = 0.38X - 0.02
Overall Precision	S = 0.53X + 0.10	S = 0.29X - 0.84	S = 1.01X - 0.26	S = 0.65X + C.32
4 <i>ccuracy</i>	X = 0.55C - 2.26	X = 0.71C + 0.47	X = 0.30C - 0.13	X = 0.59C - 4.02
Surface Water				
Single-Analyst Precision	SR = 0.45X - 0.59	SR = 0.26X - 0.88	SR = 0.75X - 0.98	SR = 0.15X + 2.12
Overall Precision	S = 0.57X - 0.26	S = 0.32X - 0.92	S = 1.07X - 0.88	S = 0.66X - 1.32
Accuracy	X = 0.51C - 1.69	X = 0.69C + 0.84	X = 0.29C + 0.50	X = 0.60C + 0.78
Industrial Effluent				
Single-Analyst Precision	SR = 0.32X + 0.65	SR = 0.26X - 0.18	SR = 0.70X - 0.35	SR = 0.46X - 2.89
Overall Precision	S = 0.75X + 0.09	S = 0.33X - 0.23	S = 0.89X - 0.39	S = 0.74X + 0.92
Accuracy	X = 0.49C - 1.30	X = 0.67C + 1.29	X = 0.35C - 0.63	X = 0.57C - 1.58

Table 1 - 11. Regression Equations for Accuracy and Precision for Compounds 13

Water Type	Fluorene	Heptachlor Epoxide	Hexachlorobutadiene	Hexachloroethane
Applicable Conc. Range -µg/L	(5.4 - 411.0)	(7.2 - 548.0)	(9.0 - 685.0)	(6.3 - 480.0)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.12X + 0.26 S = 0.13X + 0.61 X = 0.90C - 0.00	SR = 0.33X - 0.46 S = 0.28X + 0.64 X = 0.92C - 1.87	SR = 0.19X + 0.92 S = 0.26X + 0.49 X = 0.71C - 1.01	SR = 0.17X + 0.67 S = 0.17X + 0.80 X = 0.73C - 0.83
Tap Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.10X + 0.53 S = 0.13X + 0.56 X = 0.83C + 0.30	SR = 0.16X + 0.55 S = 0.36X - 0.15 X = 0.88C - 1.80	SR = 0.16X + 0.86 S = 0.16X + 1.22 X = 0.63C - 0.74	SR = 0.21X + 0.60 S = 0.21X + 0.56 X = 0.68C - 0.23
Surface Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.23X - 0.47 S = 0.27X - 0.20 X = 0.78C + 0.30	SR = 0.24X - 0.08 S = 0.35X - 0.18 X = 0.85C - 0.69	SR = 0.19X + 0.09 S = 0.21X + 0.87 X = 0.62C - 0.10	SR = 0.29X - 0.54 S = 0.26X + 0.44 X = 0.69C - 0.70
Industrial Effluent Single-Analyst Precision Overall Precision Accuracy	SR = 0.14X + 1.20 S = 0.25X + 0.92 X = 0.72C + 1.26	SR = 0.42X + 0.15 S = 0.42X + 0.05 X = 0.69C - 1.03	SR = 0.23X + 0.88 S = 0.28X + 1.06 X = 0.59C + 0.11	SR = 0.20X + 0.39 S = 0.23X + 1.02 X = 0.69C - 0.24

Table 1-12. Regression Equations for Accuracy and Precision for Compounds 17

Water Type	Indeno(1,2,3-C,D)Pyrene	N-Nitrosodi-N-Propylamine	Nitrobenzene	Phenanthrene
Applicable Conc. Range -μg/L	(7.4 - 292.0)	(18.0 - 527.0)	(9.0 - 685.0)	(9.0 - 685.0)
Distilled Water				
Single-Analyst Precision	SR = 0.29X + 1.46	SR = 0.27X + 0.68	SR = 0.19X + 0.92	SR = 0.12X + 0.57
Overall Precision	S = 0.50X + 0.44	S = 0.44X + 0.47	S = 0.27X + 0.21	S = 0.15X + 0.25
Accuracy	X = 0.78C - 3.10	X = 1.12C - 6.22	X = 1.09C - 3.05	X = 0.87C - 0.06
Tap Water				
Single-Analyst Precision	SR = 0.26X + 0.18	SR = 0.30X + 3.39	SR = 0.14X + 0.92	SR = 0.09X - 0.04
Overall Precision	S = 0.50X + 0.57	S = 0.44X + 2.69	S = 0.28X + 0.81	S = 0.10X + 0.23
Accuracy	X = 0.58C - 2.55	X = 1.09C - 8.18	X = 1.01C - 3.19	X = 0.78C + 0.73
Surface Water				
Single-Analyst Precision	SR = 0.53X - 0.20	SR = 0.43X - 3.07	SR = 0.34X - 2.25	SR = 0.16X - 0.24
Overall Precision	S = 0.57X + 0.21	S = 0.55X - 3.33	S = 0.34X + 0.84	S = 0.19X - 0.35
Accuracy	X = 0.49C - 1.73	X = 1.03C - 3.35	X = 0.97C - 1.13	X = 0.75C + 1.40
Industrial Effluent				
Single-Analyst Precision	SR = 0.36X + 0.49	SR = 0.36X + 1.77	SR = 0.18X + 1.58	SR = 0.12X + 0.94
Overall Precision	S = 0.60X + 0.08	S = 0.47X + 1.52	S = 0.34X - 0.11	S = 0.29X - 0.06
Accuracy	X = 0.54C - 1.91	X = 0.88C + 0.64	X = 1.01C - 2.70	X = 0.81C + 1.08

X = Mean Recovery C = True Value for the Concentration

X = Mean Recovery C = True Value for the Concentration

X = Mean Recovery C = True Value for the Concentration

Table 1-13. Regression Equations for Accuracy and Precision for Compounds 21				
Water Type	Pyrene	1,2-Dichlorobenzene	1,2,4-Trichlorobenzene	1,4-Dichlorobenzene
Applicable Conc. Range -µg/L	(4.5 - 343.0)	(5.4 - 411 0)	(100 - 6220)	(11.0 - 646 0)
Distilled Water				
Single-Analyst Precision	SR = 0.16X + 0.06	SR = 0.20X + 0.47	SR = 0.15X + 0.85	SR = 0 24X + 0.23
Overall Precision	S = 0.15X + 0.31	S = 0.24X + 0.39	S = 0.21X + 0.39	S = 0.29X + 0.36
Accuracy	X = 0.84C - 0.16	X = 0.80C + 0.28	X = 0.94C - 0.79	X = 0.73C - 1.47
Tap Water				
Single-Analyst Precision	SR = 0.10X + 0.22	SR = 0.17X + 1.00	SR = 0 16X + 0.11	SR = 0 18X + 0 03
Overall Precision	S = 0.13X + 0.50	S = 0.25X + 0.93	S = 0.23X + 0.67	S = 0.32X - 0.00
Accuracy	X = 0.76C - 0.06	X = 0.78C + 0.54	X = 0.80C - 0.04	X = 0.75C - 1.90
Surface Water				
Single-Analyst Precision	SR = 0.16X - 0.17	SR = 0.28X - 0.36	SR = 0.19X + 0.27	SR = 0.30X - 1 14
Overall Precision	S = 0.18X + 0.26	S = 0.25X + 1.46	S = 0.20X + 1.60	S = 0.31X - 0.19
Accuracy	X = 0.73C + 0.39	X = 0.75C + 1.18	X = 0.78C + 0.44	X = 0.68C - 1.37
Industrial Effluent				
Single-Analyst Precision	SR = 0.17X + 0.16	SR = 0.25X - 0.05	SR = 0.13X + 1.04	SR = 0.22X + 0.21
Overall Precision	S = 0.36X + 0.51	S = 0.35X + 0.26	S = 0 24X + 0.48	S = 0.30X + 0.15
Accuracy	X = 0.69C + 1.52	X = 0.73C + 1.21	X = 0.81C + 0.01	X = 0.70C - 0.65

Table 1 - 14. Regression Equations for Accuracy and Precision for Compounds 25

Water Type	2-Chloronaphthalene	2,4-Dinitrotoluene	4-Bromophenyl Phenyl Ether	4,4 -DDT
Applicable Conc Range -µg/L	(4.5 - 342.0)	(11.0 - 646.0)	(7.2 - 548 0)	(70 - 5480)
Distilled Water Single-Analyst Precision	SR = 0.07X + 0.52	SR = 0.12X + 1.06	SR = 0.13X + 0.66	SR = 0.42X + 0.19
Overall Precision Accuracy	S = 0.07X + 0.02 S = 0.13X + 0.34 X = 0.89C + 0.01	S = 0.21X + 1.50 S = 0.21X + 1.50 X = 0.92C - 4.81	S = 0.16X + 0.66 X = 0.91C - 1.34	S = 0.65X - 0.58 X = 0.79C - 3.28
Tap Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.10X + 0.32 S = 0.14X + 0.49 X = 0.85C + 0.03	SR = 0 18X + 0.89 S = 0.27X + 2.08 X = 0.83C - 2.57	SR = 0.15X + 0.23 S = 0.17X + 0.88 X = 0.85C - 1.21	$SR \approx 0.51X - 0.64$ S = 0.68X - 0.54 $X \approx 0.66C - 2.71$
Surface Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.24X + 0.28 S = 0.24X + 0.42 X = 0.79C + 0.36	SR = 0.21X + 0.46 S = 0.31X + 1.03 X = 0.83C - 2.91	SR = 0.16X + 0.22 S = 0.14X + 1.26 X = 0.83C - 0.58	SR = 0.60X - 1.16 S = 0.64X - 0.01 X = 0.56C - 2.13
Industrial Effluent Single-Analyst Precision Overall Precision Accurecy	SR = 0 15X + 0.24 S = 0.23X - 0.05 X = 0.82C + 0.63	SR = 0.11X + 2.28 S = 0.11X + 2.41 X = 0.93C - 0.64	SR = 0.21X + 0.50 S = 0.30X + 0.02 X = 0.72C - 0.19	SR = 0.46X - 0.30 S = 0.71X - 0.42 X = 0.53C - 2.12

Table 1-15. Regression Equations for Accuracy and Precision for Compounds 1

Water Type	Pentachlorophenol	Phenol	2-Chlorophenol	2-Methyl-4,6-Dinitrophenol*
Applicable Conc. Range -µg/L	(13.0 - 480.0)	(6.0 - 467.0)	(7.0 - 533.0)	(72 0 - 1067.0)
Distilled Water				
Single-Analyst Precision	SR = 0.24X + 3.03	SR = 0.26X + 0.73	SR = 0.18X + 1.46	SR = 0.22X + 9.86
Overall Precision	S = 0.30X + 4.33	S = 0.35X + 0.58	S = 0.28X + 0.97	S = 0.30X + 11.31
Accuracy	X = 0.93C + 1.99	X = 0.43C + 1.26	X = 0.78C + 0.29	X = 1.05C - 33.88
Tap Water				
Single-Analyst Precision	SR = 0.38X - 0.69	SR = 0.24X + 1.50	SR = 0.23X + 0.77	$SR \approx 0.26X + 9.38$
Overall Precision	S = 0.38X + 3.79	S = 0.43X + 0.64	S = 0.32X + 0.27	$S \approx 0.36X + 11.44$
Accuracy	X = 0.82C + 3.68	X = 0.44C + 1.14	X = 0.75C + 0.16	X = 0.99C - 28.14
Surface Water				
Single-Analyst Precision	SR = 0 19X + 0.33	$SR \approx 0.23X + 0.47$	SR = 0.17X + 0.16	SR = 0.24X - 2.78
Overall Precision	S = 0.30X + 2.10	S = 0.28X + 0.63	S = 0.24X - 0.16	S = 0.40X + 6.33
Accuracy	X = 0.85C + 2.89	X = 0.47C + 1.11	X = 0.75C - 0.07	X = 1.10C - 22.92
Industrial Effluent				
Single-Analyst Precision	SR = 0.18X + 1.09	SR = 0.27X - 0.19	SR = 0.14X - 0.35	SR = 0.23X - 5.99
Overall Precision	S = 0.26X + 4.51	S = 0.35X - 0.05	S = 0.21X + 0.48	S = 0.41X + 3.52
Accuracy	X = 0.73C + 3.38	X = 0.44C + 1.37	X = 0.72C + 0.63	$X = 1.01C \cdot 14.22$

X = Mean Recovery C = True Value for the Concentration

X = Mean Recovery C = True Value for the Concentration

X = Mean Recovery
C = True Value for the Concentration
*Revised regression equations and estimates of accuracy and precision are given in Table 13

Water Type	2-Nitrophenol	2,4-Dichlorophenol	2.4-Dimethylphenol	2,4-Dinitrophenol*
Applicable Conc. Range -μg/L	(14.0 - 520.0)	(8.0 - 600.0)	(9.0 - 667.0)	(90.0 - 1333.0)
Distilled Water				
Single-Analyst Precision	SR = 0.16X + 1.94	SR = 0.15X + 1.25	SR = 0.16X + 1.21	SR = 0.38X + 2.39
Overall Precision	S = 0.27X + 2.60	S = 0.21X + 1.28	S = 0.22X + 1.31	S = 0.42X + 26.26
A <i>ccuracy</i>	X = 1.07C - 1.15	X = 0.87C + 0.13	X = 0.71C + 4.41	X = 1.55C - 100.90
Tap Water				
Single-Analyst Precision	SR = 0.19X + 1.93	SR = 0.19X + 0.67	SR = 0.24X + 0.71	SR = 0.33X + 6.15
Overall Precision	S = 0.24X + 2.32	S = 0.24X + 1.00	$S = 0.38\dot{X} + 1.71$	S = 0.48X + 13.01
Accuracy	X = 0.95C - 0.46	X = 0.82C + 0.57	X = 0.58C + 1.13	X = 1.48C - 98.47
Surface Water				
Single-Analyst Precision	SR = 0.17X + 0.24	SR = 0.14X + 0.33	SR = 0.30X - 0.58	SR = 0.28X + 1.15
Overall Precision	S = 0.26X + 2.27	S = 0.22X + 0.82	S = 0.41X - 0.41	S = 0.30X + 26.92
Accuracy	X = 0.97C - 0.78	X = 0.89C + 0.01	X = 0.62C + 2.10	X = 1.56C - 85.38
ndustrial Effluent				
Single-Analyst Precision	SR = 0.15X + 0.77	SR = 0.17X - 0.24	SR = 0.29X + 0.10	SR = 0.25X + 6.45
Overall Precision	S = 0.33X + 1.66	S = 0.23X + 0.46	S = 0.59X - 0.15	S = 0.36X + 22.05
Accuracy	X = 0.90C + 0.78	X = 0.81C + 0.61	X = 0.49C + 1.91	X = 1.24C - 54.41

Table 1-17. Regression Equations for Accuracy and Precision for Compounds 9

Water Type	2,4,6-Trichlorophenol	4-Chloro-3-Methylphenol	4-Nitrophenol
Applicable Conc. Range -μg/L	(11.9 - 440.0)	(9.0 - 667.0)	(21.6 - 800.0)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.16X + 2.22 S = 0.22X + 1.81 X = 0.91C - 0.18	SR = 0.23X + 0.75 S = 0.29X + 1.31 X = 0.84C + 0.35	SR = 0.38X + 2.57 S = 0.44X + 3.24 X = 0.61C - 1.22
Tap Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.17X + 2.35 S = 0.19X + 1.85 X = 0.88C + 1.26	SR = 0.18X + 1.49 S = 0.27X + 1.33 X = 0.77C + 0.67	SR = 0.28X+2.44 S = 0.44X+2.09 X = 0.56C-2.16
Surface Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.16X + 0.42 S = 0.28X + 0.92 X = 0.88C - 0.36	SR = 0.18X + 0.30 S = 0.28X + 1.28 X = 0.81C - 0.03	SR = 0.31X - 0.33 S = 0.43X + 2.90 X = 0.58C + 0.74
Industrial Effluent Single-Analyst Precision Overall Precision Accuracy	SR = 0.08X + 3.09 S = 0.23X + 1.35 X = 0.82C + 1.36	SR = 0.14X + 1.31 S = 0.27X + 1.46 X = 0.76C + 0.95	SR = 0.43X - 2.96 S = 0.39X + 5.09 X = 0.52C + 7.02

Table 2. Revised Regression Equations for Accuracy and Precision

Water Type	2-Methyl-4,6-Dinitrophenol	2,4-Dinitrophenol
Applicable Conc. Range -µg/L	(144 - 1067)	(90 - 2666)
Distilled Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.05X + 42.29 S = 0.26X + 23.10 X = 1.04C - 28.04	SR = 0.38X + 2.36 S = 0.42X + 26.29 X = 0.81C - 18.04
Tap Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.15X + 0.38 S = 0.31X + 23.39 X = 1.00C - 29.72	SR = 0.33X + 6.20 S = 0.48X + 13.02 X = 0.82C - 24.25
Surface Water Single-Analyst Precision Overall Precision Accuracy	SR = 0.11X + 0.66 S = 0.35X + 21.03 X = 1.07C - 13.19	SR = 0.28X + 1.15 S = 0.29X + 26.97 X = -0.87C + 8.09
Industrial Effluent Single-Analyst Precision Overall Precision Accuracy	SR = 0.15X - 26.29 S = 0.42X - 2.86 X = 0.96C + 0.41	SR = 0.25X + 6.43 S = 0.36X + 22.11 X = 0.68C + 7.82

X = Mean Recovery C = True Value for the Concentration *Revised regression equations and estimates of accuracy and precision are given in Table 13

X = Mean Recovery C = True Value for the Concentration

X = Mean Recovery C = Prepared Concentration

of 21%. One-half of the RSD-SAs for the acid compounds are between 17% and 30%. In 95% of the cases, the RSD-SAs are less than 43%.

The effect of water type was different for the various base/neutral and acid compounds. For most compounds, the water matrix does not have a great effect on either the accuracy or precision. Overall, recoveries for the base/neutral compounds averaged 81% in distilled water, 74% in tap water, 71% in surface water, and 69% in the industrial effluent matrix. Recoveries for the acid compounds averaged 77% in distilled water, 71% in tap water, 77% in surface water, and 72% in the industrial effluent. Precision (RSD and RSD-SA) for the base/neutral compounds tended to be poorer for the surface water and industrial effluent (median RSD = 38% and median RSD-SA 28%) than the distilled and tap water (median RSD = 32% and median RSD-SA = 22%). Precision for the acid compounds tended to be poorer for the tap water (median RSD = 41% and median RSD-SA = 25%) than for the distilled water, surface water and industrial effluent (median RSD = 32% and median RSD-SA = 19%).

Conclusions and Recommendations

It is highly recommended that the column be checked for resolution of compounds, peak geometry (tailing), and total response of the compound. An improperly performing column can lead to problems of misidentification and poor accuracy and precision of the reported values. Suggested compounds for checking the column include: 1.3dichlorobenzene (7.4 min) and 1,4dichlorobenzene (7.8 min) for the early eluters, acenaphthylene (17.4 min) and acenaphthene (17.8 min) for the middle eluters; and chrysene (31.5 min) and din-octylphthalate (32.5 min) for the late eluting compounds. For the acids, 2,4dinitrophenol (15.9 min) and 2-methyl-4,6-dinitrophenol (16.2 min) are suggested.

Excessive tailing may be minimized by coating contact surfaces with phosphoric acid or a weak organic acid.

Some laboratories reported problems with nonlinearity and poor response with the following compounds: nitrophenols, pentachlorophenol, aldrin, DDT, DDD, DDE and BHC isomers. It is recommended that the analyst should prepare one of the standards used for the standard curve close in response to the sample response.

It is recommended that the retention times be checked, especially for the highly polar compounds, by frequent use of standards.

Multiple internal standards, such as deuterated naphthalene, phenanthene, and chrysene, were recommended by several of the participating laboratories.

It is recommended that a pure DDT standard be used to detect possible degradation of DDT to DDD or DDE.

It is suspected that the low molecular weight phthalate esters may hydrolyze under basic conditions used in the extraction procedure. It is recommended that this step be performed as quickly as possible.

This Project Summary was prepared by staff of Radian Corporation, Austin, TX 78766.

Raymond Wesselman and Robert L. Graves are the EPA Project Officers (see below).

The complete report, entitled "EPA Method Study 30, Method 625—Base/ Neutrals, Acids and Pesticides," (Order No. PB 84-206 572; Cost: \$34.00, subject to change) will be available only from:

National Technical Information Service 5285 Port Royal Road

Springfield, VA 22161 Telephone: 703-487-4650

The EPA Project Officers can be contacted at:

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